(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 719 847 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
03.07.1996 Bulletin 1996/27

(21) Application number: **95916048.2**

(22) Date of filing: **25.04.1995**

(51) Int. Cl.[6]: **C09D 11/00**, B41M 5/00

(86) International application number:
PCT/JP95/00815

(87) International publication number:
WO 95/29208 (02.11.1995 Gazette 1995/47)

(84) Designated Contracting States:
CH DE FR GB IT LI NL SE

(30) Priority: **25.04.1994 JP 86731/94**
25.04.1994 JP 86732/94

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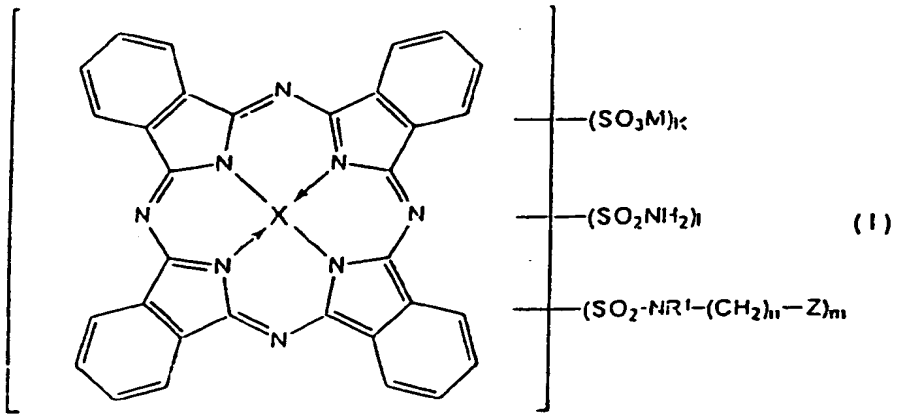
(54) WATER-BASE INK COMPOSITION AND METHOD OF RECORDING THEREWITH

(57) A cyan ink comprising a phthalocyanine derivative represented by the following formula (I), excellent in color reproducibility, suitable for use in the ink jet recording method is disclosed. The combination use of this cyan ink comprising the phthalocyanine derivative with yellow and magenta inks, each comprising a specific dye, gives excellent color printing.



(I)

wherein X represents an ion of a metal selected from Cu, Fe, Co and Ni, R^1 represents H or an alkyl group, Z represents -OH, -COOH or NR^2R^3 (where R^2 represents H or an alkyl group, and R^3 represents an alkyl group or phenyl group), n represents an integer of 1 to 15, k and l represent 0 or 1, and m represents an integer of 1 to 4, provided that k, l and m fulfill the inequality $2 \leq k + l + m \leq 4$.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an ink composition for recording, and to a method of recording, in particular, an ink jet recording method, using the same. More particularly, the present invention relates to an ink composition comprising as a colorant a phthalocyanine derivative, to a method of recording, in particular, an ink jet recording method, using the same, and to a method for forming color images.

Background Art

Ink compositions are required to have various excellent properties. Specifically, they are not only required to have excellent color reproducibility, but also required to produce images which are excellent in water resistance and light resistance.

Further, in the ink jet recording method in which droplets of an ink composition are ejected on a recording medium to form thereon an image, the ink composition is required to have much more excellent properties than those required for ordinary writing utensils such as fountain pens and ball-point pens. For instance, the ink composition is required to have a proper viscosity and a suitable surface tension, to be excellent in preservation stability, and not to cause clogging in a nozzle.

In general, many of these properties required for the ink composition for use in the ink jet recording method can be fulfilled by an aqueous ink composition comprising a water- soluble dye, water and a water-soluble organic solvent. The properties of printed images, such as color tone, water resistance and light resistance, are highly dependent on the dye used. It has been tried to utilize various dyes.

Ink compositions containing a phthalocyanine derivative as a cyan or blue dye have been proposed. For instance, the use of C.I. Direct Blue 86, 87 or 199 has been proposed. Further, the use of a phthalocyanine derivative is also disclosed, for example, in Japanese Laid-Open Patent Publications Nos. 2772/1986, 149758/1987, 190273/1987 and 200883/1991.

However, there is yet room for improvement in these ink compositions containing a phthalocyanine derivative.

On the other hand, such a printer that produces color images by means of the ink jet printing method is also popular. Color images are formed by using, in general, yellow, magenta and cyan ink compositions, and optionally a black ink composition. By superposing these ink compositions, red, green, and blue, and optionally black colors are developed. In such color printing, each ink composition is required to be highly reproducible in its own color. In addition to this, these ink compositions are required to be excellent in reproducibility in red, green, and blue, and optionally black colors which are developed by superposing ink compositions one over another.

SUMMARY OF THE INVENTION

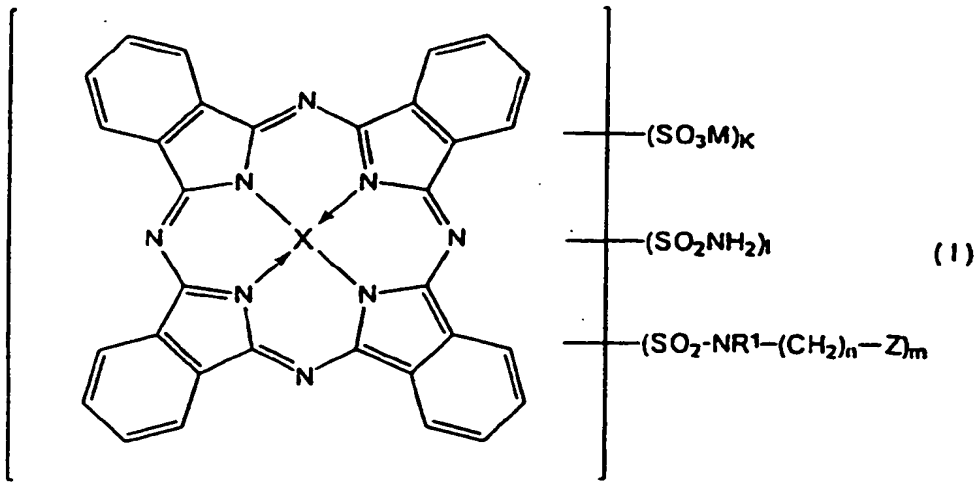
We have now found that an ink composition comprising as a colorant a specific phthalocyanine derivative has extremely excellent properties. Furthermore, we have also found that excellent color printing can be obtained by the use of the combination of this cyan ink composition with yellow and magenta ink compositions, each comprising a specific dye.

Accordingly, an object of the present invention is to provide an ink composition having various properties which are required for ink compositions.

Another object of the present invention is to provide an ink composition having various properties which are required for ink compositions useful for ink jet recording.

A further object of the present invention is to provide a method of printing, in particular, an ink jet recording method, by which excellent color images can be obtained.

According to the present invention, there provides a cyan ink composition comprising as a colorant a phthalocyanine derivative represented by the following formula (I):



(I)

wherein

X represents an ion of a metal selected from Cu, Fe, Co and Ni,

M represents hydrogen atom, an alkaline metal, ammonium or an organic amine,

R^1 represents hydrogen atom or an alkyl group which may be substituted,

Z represents -OH, -COOH or NR^2R^3 (where R^2 represents hydrogen atom or an alkyl group which may be substituted, and R^3 represents an alkyl group which may be substituted, or phenyl group which may be substituted),

n represents an integer of 1 to 15,

k and l each independently represent 0 or 1, and

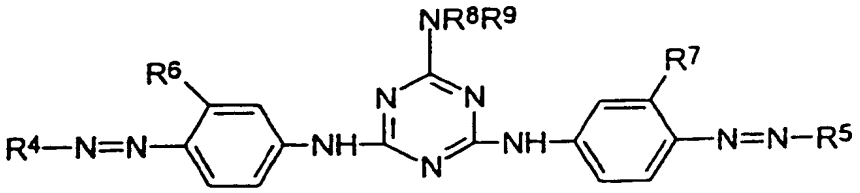
m represents an integer of 1 to 4,

provided that k, l and m fulfill the inequality $2 \leq k + l + m \leq 4$.

According to the present invention, there provides a method in which yellow, magenta and cyan ink compositions are used, wherein

the cyan ink composition comprises as a colorant the compound represented by the above formula (I),

the yellow ink composition comprises as a colorant a compound represented by the following formula (II):



(II)

wherein

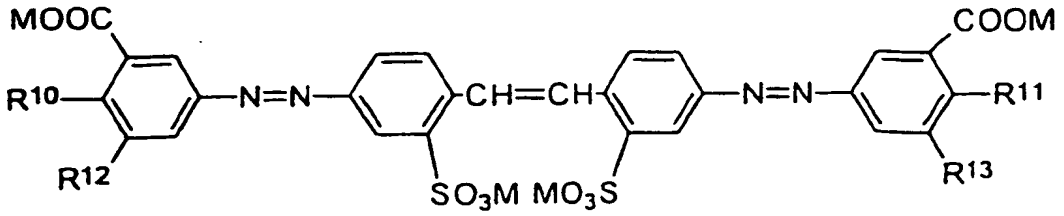
R^4 and R^5 each independently represent -OH; $-SO_3M$; or phenyl or naphthyl group substituted with -COOM,

R^6 and R^7 each independently represent hydrogen atom, an alkyl group or an alkoxy group,

R^8 represents hydrogen atom, an alkyl group or a hydroxyalkyl group,

R^9 represents hydrogen atom, -OH or a hydroxyalkyl group, and

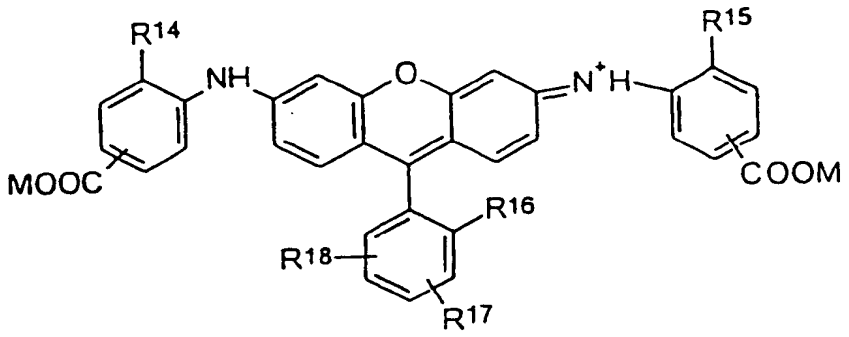
M is as defined in the above formula (I), or a compound represented by the following formula (III):



(III)

wherein

R^{10} and R^{11} each independently represent hydrogen atom, -OH or an alkoxy group,
R^{12} and R^{13} each independently represent hydrogen atom or an alkyl group, and
M is as defined in the above formula (I), and
the magenta ink composition comprises as a colorant a compound represented by the following formula (IV):



(IV)

wherein

R^{14} represents hydrogen atom or an alkyl group,
R^{15} represents hydrogen atom, a halogen atom or an alkyl group,
R^{16} represents -COOH or $-SO_3^-$,
R^{17} and R^{18} each independently represent hydrogen atom, a halogen atom, an alkyl group or $-SO_3M$, and
M is as defined in the above formula (I).

DETAILED DESCRIPTION OF THE INVENTION

Phthalocyanine Derivatives

The phthalocyanine derivative for use in the cyan ink composition according to the present invention is a compound represented by the above formula (I).

In the formula (I), hydrogen atoms on four benzene rings in the phthalocyanine skeleton are substituted with the groups $-(SO_3M)k$, $-(SO_2NH_2)l$ and $-(SO_2-NR^1-(CH_2)N-Z)m$. While the position of the substitution is not particularly limited, among the above three groups, the group $-(SO_2-NR^1-(CH_2)N-Z)m$ should exist in a number of at least one. The above groups can exist in a number of four or less in total. In other words, it is necessary that k and l represent an integer of 0 or 1, that m be an integer of 1 to 4, and that k, l and m be in the relationship which fulfills the inequality $2 \leq k+l+m \leq 4$.

In the formula (I), X represents an ion of a metal selected from Cu, Fe, Co and Ni.

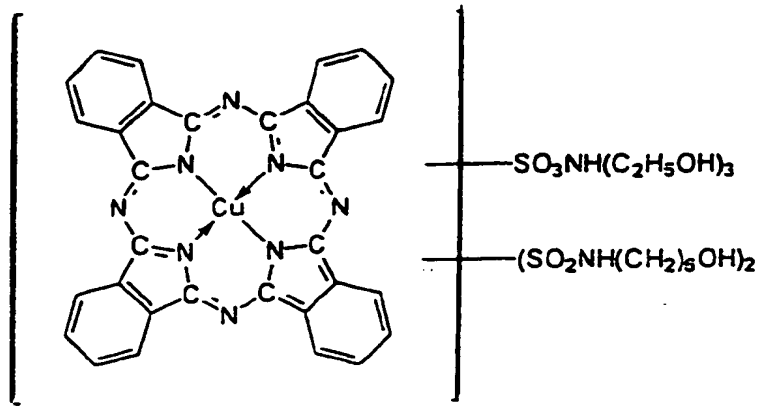
Specific examples of the alkaline metal and the organic amine represented by M in the formula (I) include lithium, sodium, potassium, ammonium, dimethylammonium, morpholium and piperidinium.

The alkyl group represented by R^1 in the formula (I) is preferably a linear or branched C_{1-4} alkyl group. One or more hydrogen atoms in this alkyl group may be substituted, and preferable examples of the substituent include hydroxyl group and amino group.

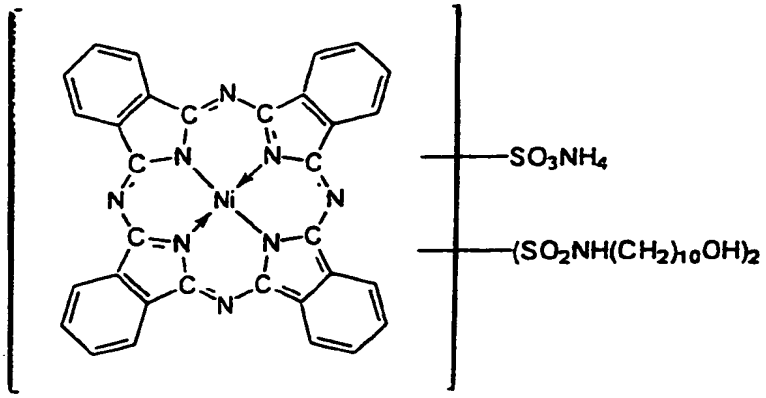
In NR^2R^3 represented by Z in the formula (I), R^2 represents hydrogen atom or an alkyl group. This alkyl group is preferably a linear or branched C_{1-4} alkyl group. One or more hydrogen atoms in this alkyl group may be substituted, and preferable examples of the substituent include hydroxyl group and amino group. Further, R^3 represents an alkyl group or phenyl group. This alkyl group is preferably a linear or branched C_{1-4} alkyl group. One or more hydrogen atoms in this alkyl group may be substituted, and preferable examples of the substituent include hydroxyl group and amino group. Furthermore, one or more hydrogen atoms on the phenyl group may be substituted, and examples of the substituent include hydroxyl group and amino group.

In the formula (I), n represents an integer of 1 to 15. However, when Z is -COOH, n is preferably an integer of 2 to 12; and when Z is -OH, n is preferably an integer of 5 to 15.

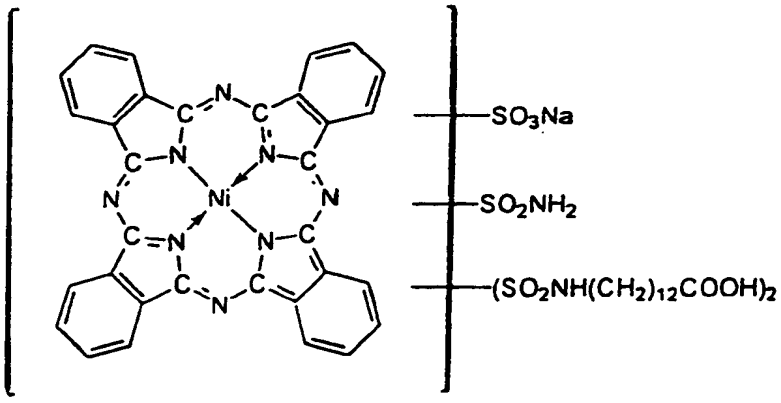
Specific preferable examples of the phthalocyanine derivative represented by the formula (I) include the following compounds (I-1) to (I-16):



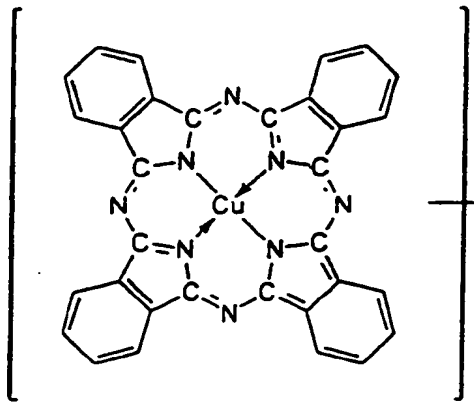
(I-1)



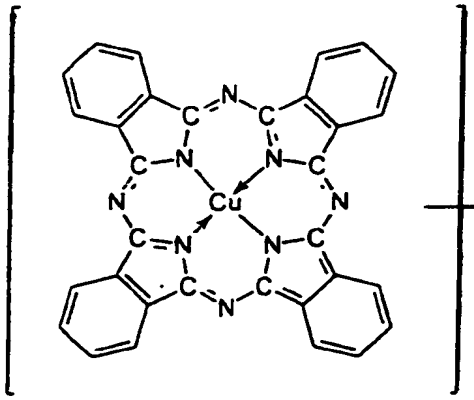
(I-2)



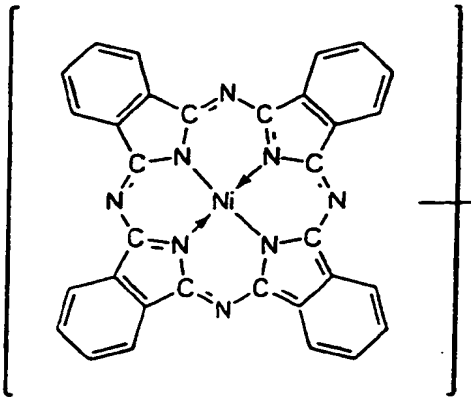
(I-3)



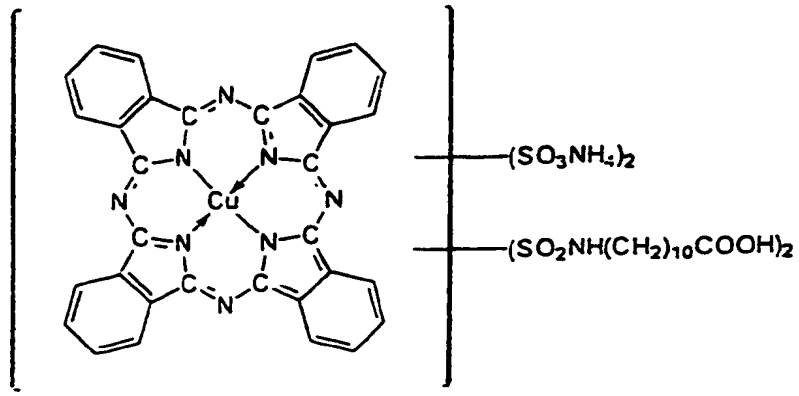
(I-4)



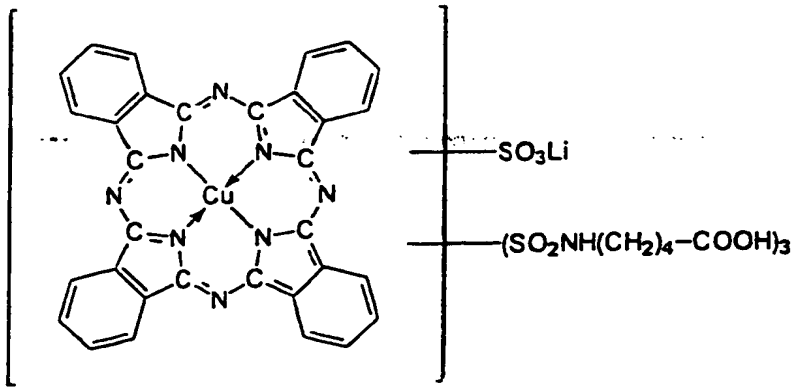
(I-5)



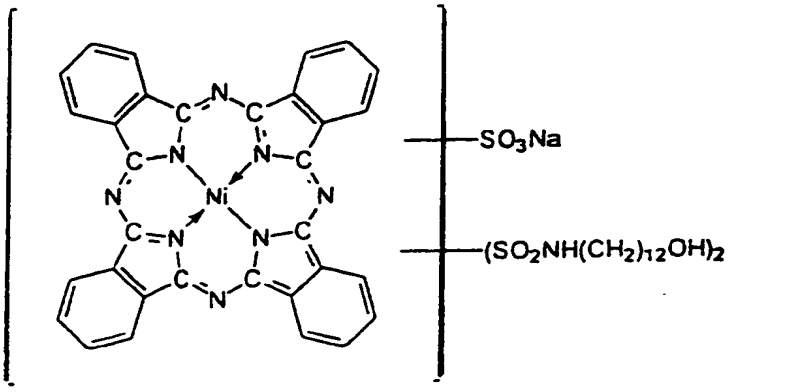
(I-6)



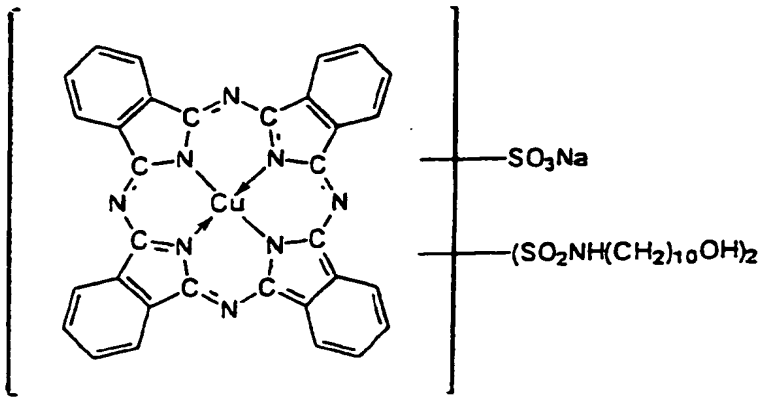
(I-7)



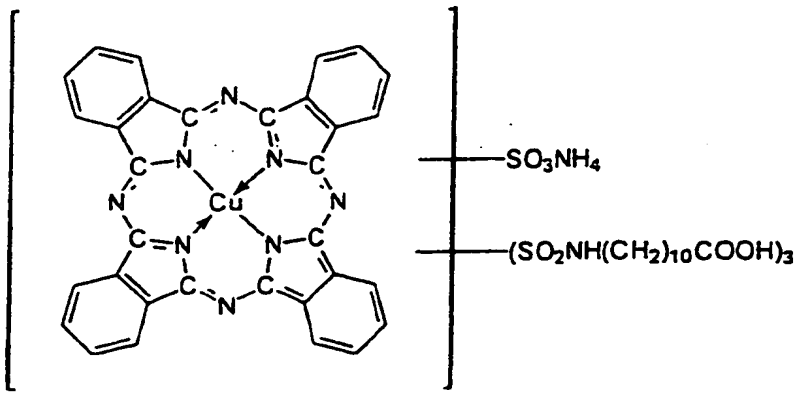
(I-8)



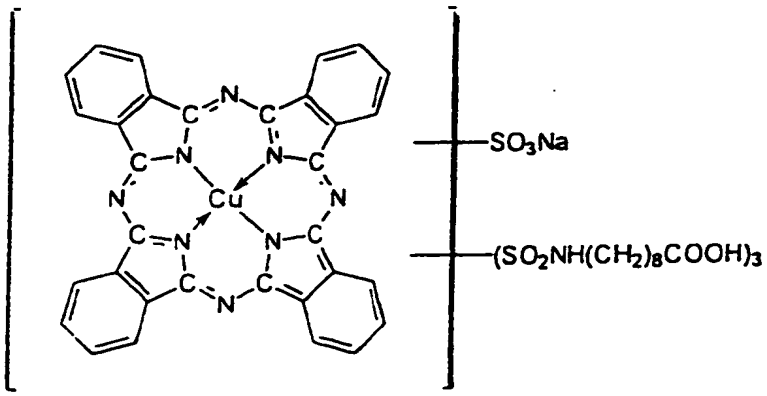
(I-9)



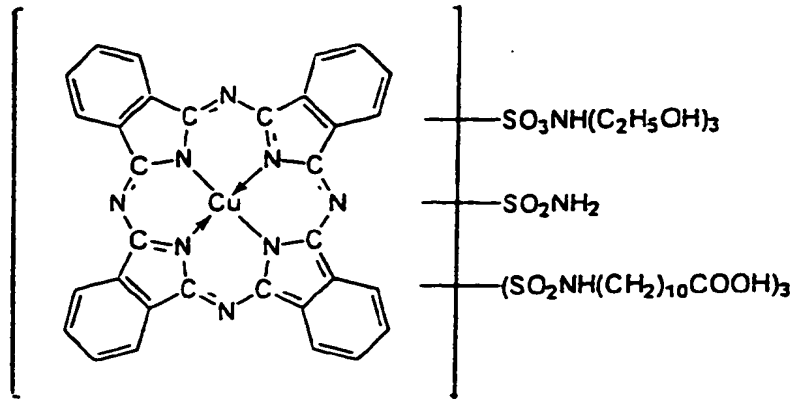
(I - 10)



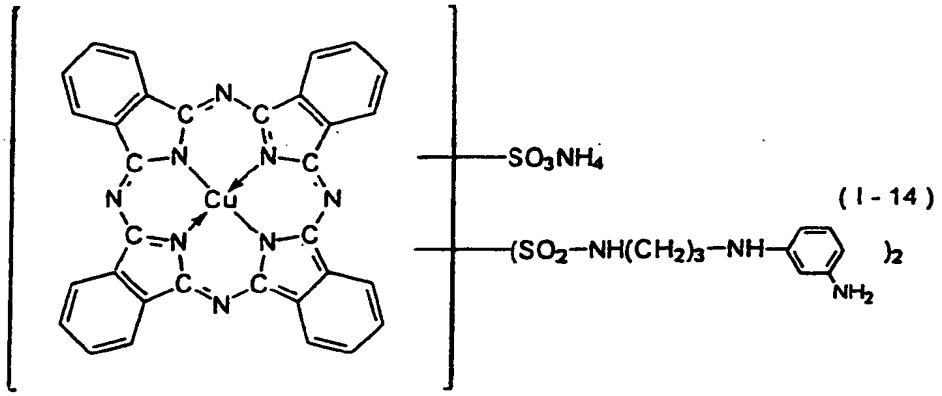
(I - 11)



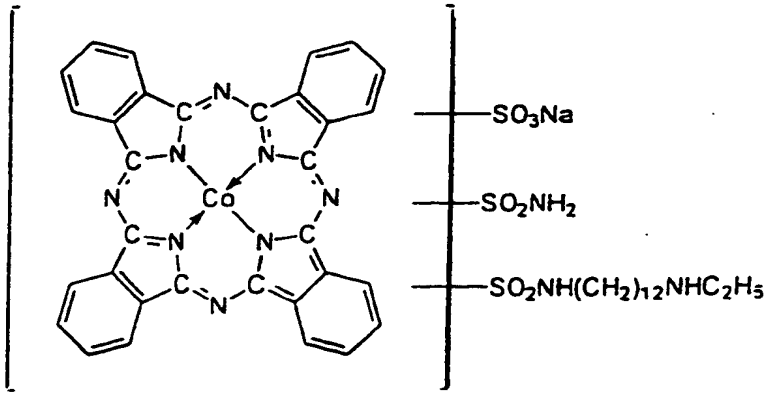
(I - 12)



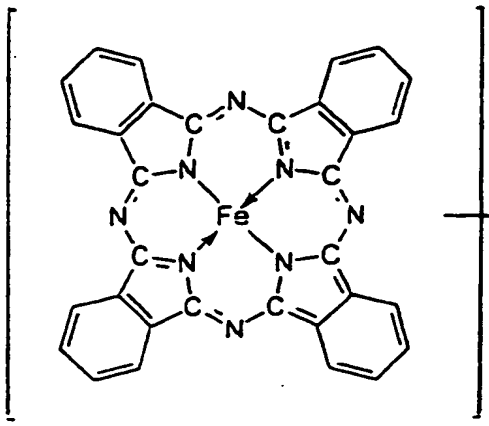
(I - 13)



(I - 14)



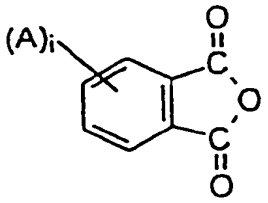
(I - 15)



(I - 16)

The compound having the formula (I) can be produced in accordance with a known method for preparing a phthalocyanine derivative. For example, the compound (I) can be obtained in accordance with the method described in Japanese Laid-Open Patent Publication No. 22967/1984 or Japanese Laid-Open Patent Publication No. 30874/1984.

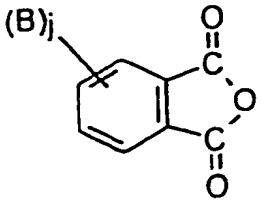
The compound having the formula (I) can be produced by the following method. The compound (I) can be prepared by reacting a compound represented by the following formula (Va):



(Va)

wherein A represents the group $-(SO_3M)k$, $-(SO_2NH_2)l$ or $-(SO_2-NR^1-(CH_2)N-Z)m$ (where M, R^1, Z, k, l and m are as defined in the formula (I)), and i represents an integer of 1 to 4, or

a mixture of the compound (Va) and a compound represented by the following formula (Vb):

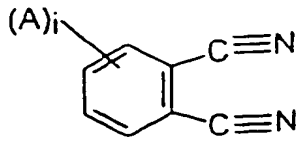


(Vb)

wherein B represents the group $-(SO_3M)k$, $-(SO_2NH_2)l$ or $-(SO_2-NR^1-(CH_2)N-Z)m$ (where M, R^1, Z, k, l and m are as defined in the formula (I)), and j represents an integer of 1 to 4, with urea and a metal chloride represented by the formula XCln (where n agrees with the valency of X). In this reaction, excessive urea dissolved may also play a role of a reaction solvent, and the reaction can be carried out at a temperature of preferably about 190 to 200°C.

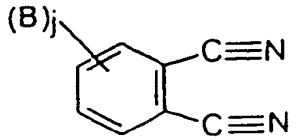
The values of k, l and m in the compound having the formula (I) can be controlled by properly selecting the type and the mixing ratio of the compounds (Va) and (Vb).

Further, the compound (I) can be prepared from a compound of the formula (VIa):



(VIa)

wherein A and i are as defined above, or the compound (VIa), and a compound of the formula (VIb):



(VIb)

wherein B and j are as defined above.
with a metal chloride represented by the formula XCln (where n agrees with the valency of X). The reaction is carried out by:

(a) mixing these compounds and heating the mixture, for example, at a temperature of approximately 150 to 200°C, or
(b) heating the mixture at a temperature of approximately 190 to 200°C in an inert solvent in the presence or absence of urea.

Also in this method, the values of k, l and m in the compound (I) can be controlled by properly selecting the type and the mixing ratio of the compounds (VIa) and (VIb).

The amount of the compound (I) to be incorporated into the ink composition can be properly determined depending upon the type of the solvent component used, the properties required for the ink. However, in the case where the ink composition will be used in the ink jet recording method, the incorporation amount of the compound (I) is preferably from 1.5 to 8.0% by weight, more preferably from 2.5 to 6.5% by weight of the ink composition from the viewpoint of color tone.

Further, a mixture of water and a water-soluble organic solvent is preferred as the solvent for use in the ink composition of the present invention. Examples of this water- soluble organic solvent include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, 1,3-propane diol, 1,5- pentane diol, 1,2,6-hexane triol and glycerol; ethers of polyhydric alcohols such as ethylene glycol monomethyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether and dipropylene glycol monomethyl ether; nitrogen-containing solvents such as formamide, dimethylformamide, diethanolamine, triethanolamine, 1,3-dimethyl-2-imidazolidinone, 2-pyrrolidone and N-methyl-2-pyrrolidone; and sulfur-containing solvents such as thiodiglycol and dimethyl sulfoxide.

These solvents can be used either singly or as a mixture of two or more. The amount of the solvent is in the range of 3 to 40% by weight, preferably in the range of 3 to 30% by weight of ink composition from the view point of the prevention of clogging in a nozzle and the quality of images printed.

Further, in order to enhance the drying characteristics of the ink after the formation of an image, it is preferable that the ink composition of the present invention further comprise a lower alcohol such as ethanol, 1-propanol or 2-propanol; an anionic surface active agent such as a fatty acid salt or an alkylsulfate ester; or a nonionic surface active agent such as acetylene glycol, a polyoxyethylene alkyl ether or a polyoxyethylene fatty ester. From the viewpoint of the quality of images printed, the amount of the lower alcohol to be incorporated is preferably in the range of 2 to 10% by weight, more preferably in the range of 2 to 6% by weight of the ink composition. The amount of the surface active agent to be incorporated is preferably in the range of 0.01 to 2% by weight of the ink composition.

The ink composition according to the present invention may further comprise a water-soluble polymer or resin, an anti- foaming agent, a pH modifier, a mildew-proofing agent and the like, if necessary.

The ink composition of the invention can be produced in a conventional manner. For instance, the ink can be obtained by the following method: all of the components are thoroughly mixed and dissolved, and the mixture is filtered under pressure through a membrane filter having a hole diameter of 0.8 micrometers, and then degased by using a vacuum pump.

The ink composition according to the present invention is particularly suitable for use in the ink jet recording method in which an ink is ejected through a fine pore as droplets to conduct recording. The ink composition of the invention can also be used for ordinary writing utensils, recorders, pen plotters and the like.

In the case of the ink jet recording method, it is possible to achieve excellent image recording by adopting, in particular, a means in which droplets are ejected by utilizing the vibration of a piezoelectric device, or a means in which thermal energy is utilized.

Formation of Color Images

According to another preferred embodiment of the present invention, there is provided a method for producing color images, in which the ink composition comprising the compound (I) above described, and specific yellow and magenta ink compositions are used.

The yellow ink composition for use in this embodiment comprises as a colorant a compound represented by the above formula (II) or (III). Further, the magenta ink composition for use in this embodiment comprises as a colorant a compound represented by the above formula (IV).

By using these ink compositions in combination, color images whose colors are well reproduced can be formed. These ink compositions are highly reproducible in their own colors, and, in addition to this, they are excellent in reproducibility in red, green, blue and black colors which are obtained by superposing two of or all of the ink compositions one over another.

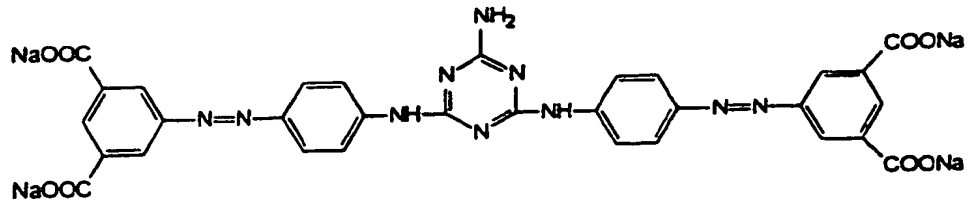
In the formula (II), one or more hydrogen atoms in the phenyl or naphthyl group represented by R^4 or R^5 may be substituted. Specific examples of the substituent include hydroxyl group, $-SO_3M$, $-COOM$, $-PO_3M_2$ (where M is as defined above), an alkyl group (preferably a C_{1-4} alkyl group), and an alkoxy group (preferably a C_{1-4} alkoxy group).

In the formula (II), the alkyl group represented by R^6 or R^7 is preferably a linear or branched C_{1-3} alkyl group. The alkoxy group represented by R^6 or R^7 is preferably a linear or branched C_{1-4} (preferably C_{1-2}) alkoxy group.

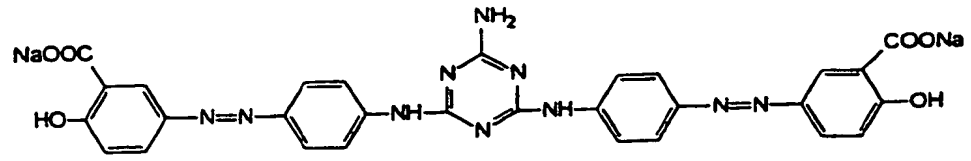
The alkyl group represented by R^8 is preferably a linear or branched C_{1-3} alkyl group. The alkyl moiety of the hydroxyalkyl group represented by R^8 is a linear or branched C_{1-4} (preferably C_{1-2}) alkyl group.

Further, the alkyl moiety of the hydroxyalkyl group represented by R^9 is a linear or branched C_{1-4} (preferably C_{1-2}) alkyl group.

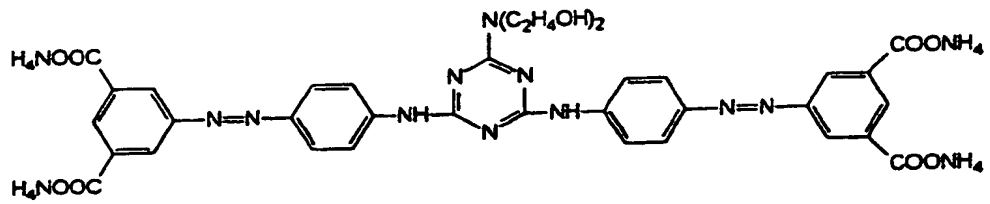
Specific preferable examples of the compound represented by the formula (II) include the following compounds (II-1) to (II-10):



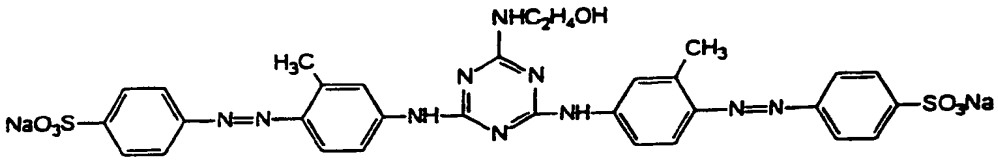
(II - 1)



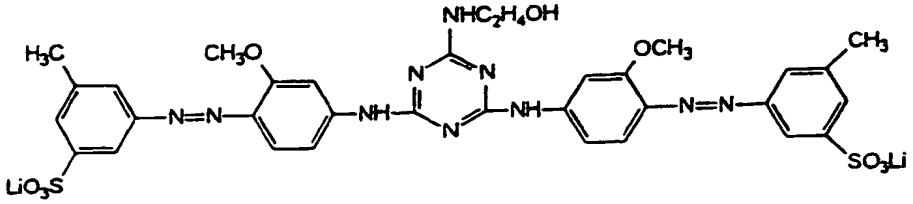
(II - 2)



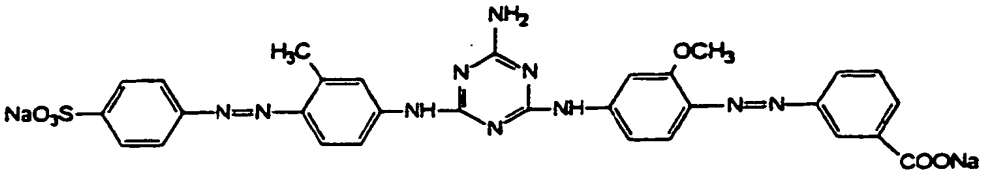
(II - 3)



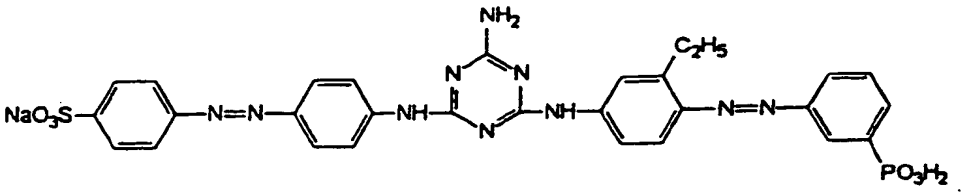
(II - 4)



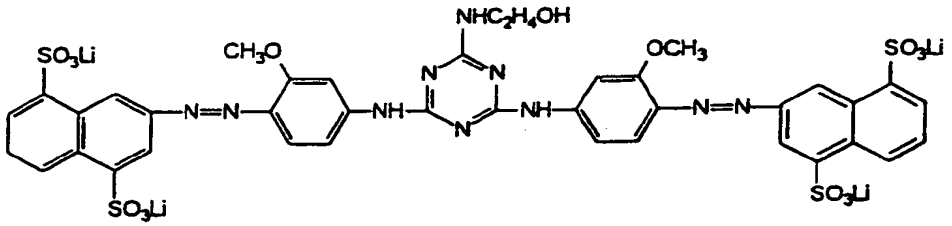
(II - 5)



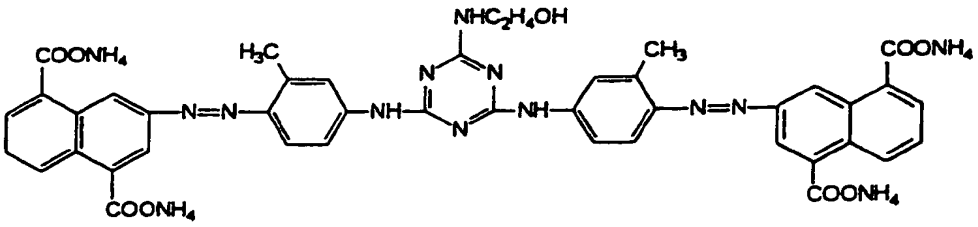
(II - 6)



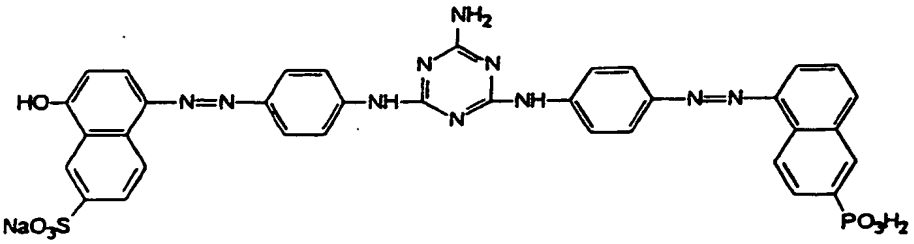
(II - 7)



(II - 8)



(II - 9)

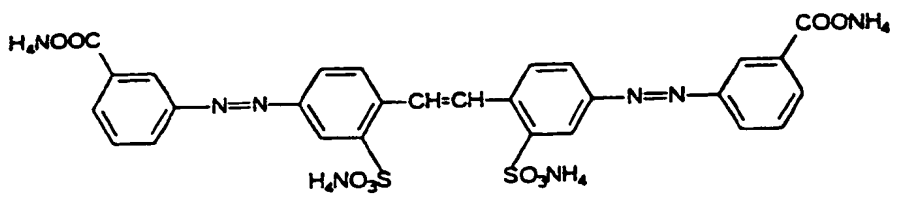


(II - 10)

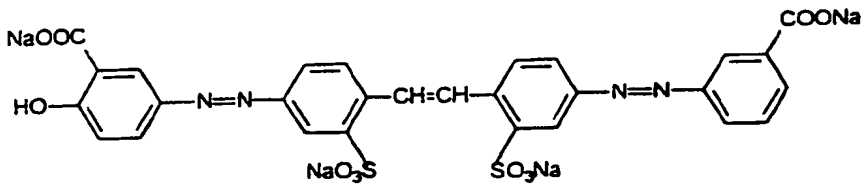
The alkoxy group represented by R^{10} or R^{11} in the formula (III) is a linear or branched C_{1-4} (preferably C_{1-2}) alkoxy group.

Further, the alkyl group represented by R^{12} or R^{13} is preferably a linear or branched C_{1-4} alkyl group.

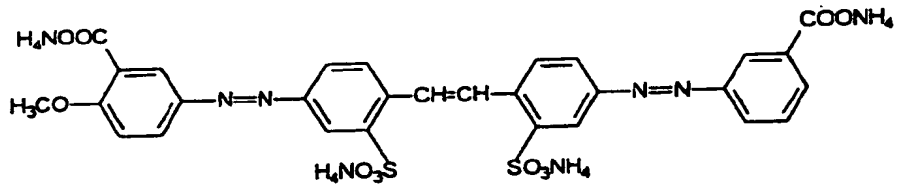
Specific preferable examples of the compound represented by the formula (III) include the following compounds (III-1) to (III-10):



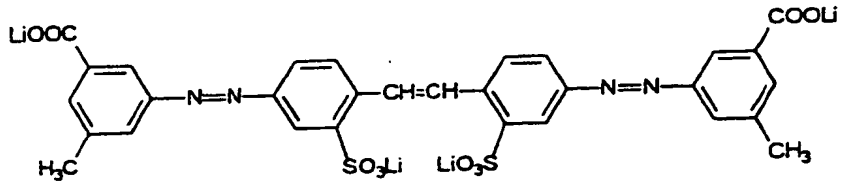
(III - 1)



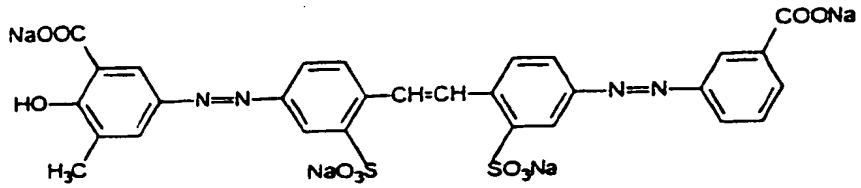
(III - 2)



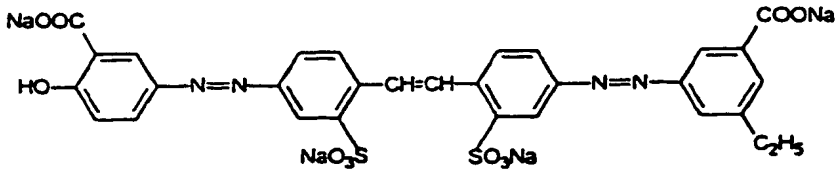
(III - 3)



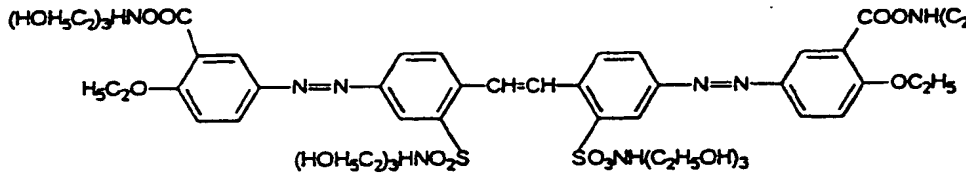
(III - 4)



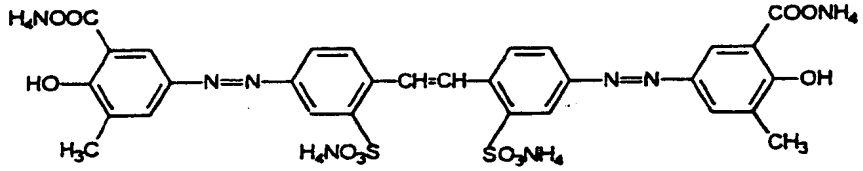
(III - 5)



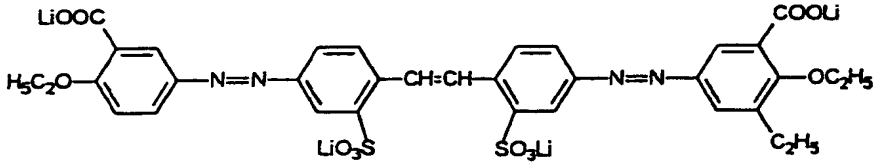
(III - 6)



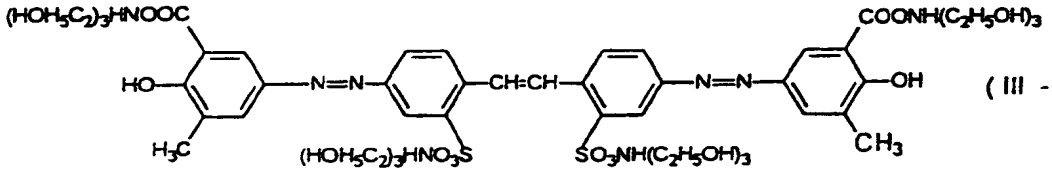
(III - 7)



(III - 8)



(III - 9)



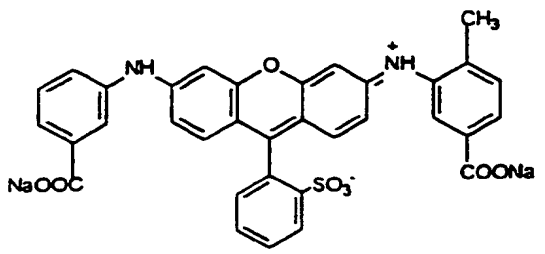
(III - 10)

The alkyl group represented by R^{14} in the formula (IV) is preferably a linear or branched C_{1-4} alkoxy group.

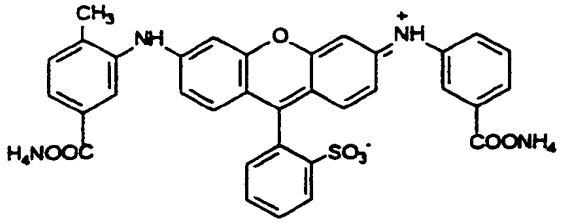
Further, the halogen atom represented by R^{15} is preferably fluorine, chlorine, bromine or iodine. Furthermore, the alkyl group represented by R^{15} is preferably a linear or branched C_{1-4} alkyl group.

The halogen atom represented by R^{17} or R^{18} is preferably fluorine, chlorine, bromine or iodine. Further, the alkyl group represented by R^{17} or R^{18} is preferably a linear or branched C_{1-4} alkyl group.

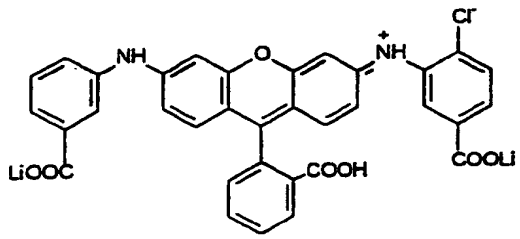
Specific preferable examples of the compound represented by the formula (IV) include the following compounds (IV-1) to (IV-10):



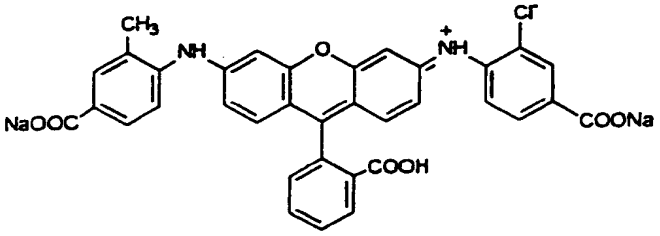
(IV - 1)



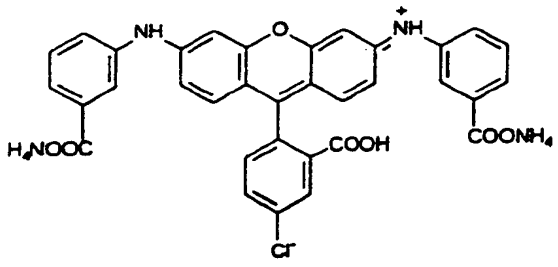
(IV - 2)



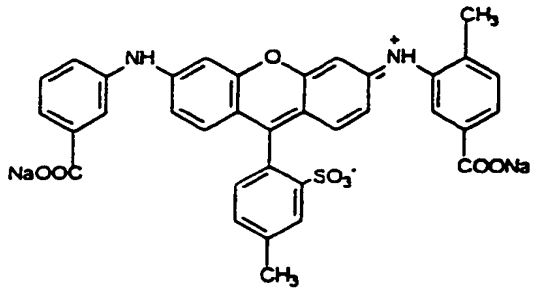
(IV - 3)



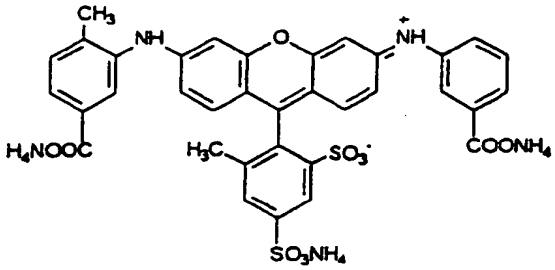
(IV - 4)



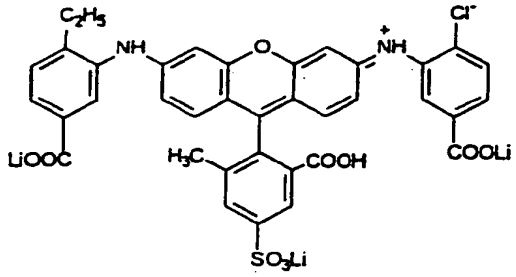
(IV - 5)



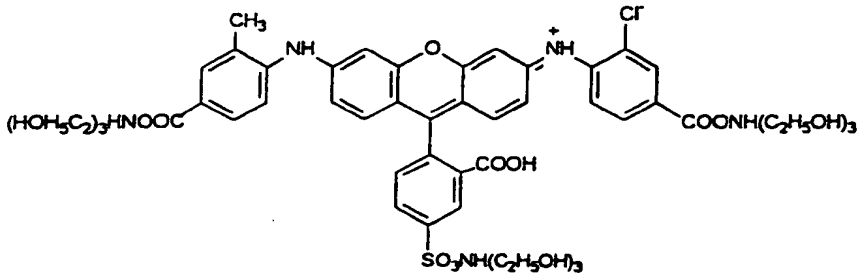
(IV - 6)



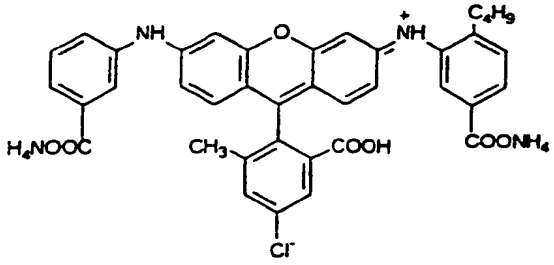
(IV - 7)



(IV - 8)



(IV - 9)



(IV - 10)

The ink composition comprising the compound (II), (III) or (IV) can be formulated and prepared in the same manner as in the case of the ink composition comprising the compound (I). According to the Preferred embodiment of the present invention, in the case where an image will be formed by the ink jet printing method, the amount of the

compound (II) or (III) to be incorporated into the ink composition is preferably about 0.5 to 3.0% by weight, more preferably about 1.0 to 2.0% by weight of the ink composition. Further, in the case of the compound (IV), the amount thereof is preferably about 0.5 to 4.0% by weight, more preferably about 1.0 to 3.0% by weight of the ink composition.

EXAMPLES

The present invention will now be explained more specifically by referring to the following Examples. However, the present invention is not limited to these examples.

Example A

Inks, each having the composition shown in Table 1 were prepared in a conventional manner. In the table, figures are in "% by weight" of the ink composition and the balances are water.

Table 1

Formulation of Ink		Example A										Comparative Example A		
		1	2	3	4	5	6	7	8	9	10	1	2	3
Dye	(I-1)	8	6	4			2				1			
	(I-5)				1.5						1			
	(I-7)					2.5	2							
	(I-8)							3.5						
	(I-9)								6.5					
	(I-11)									3				
	(I-14)										1			
	C.I. Acid Blue 9											3		
	C.I. Direct Blue 86												4	3
Ethylene glycol							10							
Diethylene glycol		40	30	10			15	17		15		10	10	
Glycerol				5	3	4			8		5	5	5	5
Diethylene glycol monobutyl ether								10						
Triethylene glycol monobutyl ether									12	10				
Triethanolamine						1		1						
2-Pyrrolidone						3								
Thiodiglycol											8			8
Ethanol						4								
1-Propanol					6						3			3
Surfynol 465*				1			0.8			1.5		1	1	
Mildew-proofing agent				0.3	0.3	0.3	0.3					0.3	0.3	

*: Surfynol 465 (manufactured by Nisshin Kagaku Kabushiki Kaisha, acetylene glycol surface active agent)

Evaluation Test A

The ink compositions of Examples A1 to A10 and of Comparative Examples A1 to A3 were evaluated in terms of the following Tests A1 to A4, by using the following printer and recording papers.

Printer

Printer (1): An ink jet printer having an on-demand-type ink jet head (diameter of nozzle: 35 micrometers, 48 nozzles) made on an experimental basis, which produces droplets by utilizing the vibration of a piezoelectric device to conduct recording; the printer can print an image under such conditions that the driving frequency is 5 kHz, that the voltage for driving the piezoelectric device is 25 V and that the resolution is 360 dots/inch.

Printer (2): Desk Writer 550C (manufactured by Hewlett Packard Corp.)

Recording Papers

(1) Coated paper NM for ink jet printing (manufactured by Mitsubishi Paper Mills)
(2) Canon Dry (manufactured by Canon Hanbai)
(3) Xerox 4024 (manufactured by Xerox)
(4) Xerox P (manufactured by Fuji Xerox)
(5) Ricopy 6200 (manufactured by Ricoh)

Test A1: Color Reproducibility

A solid image (100% duty) was printed by the printer (1) on each of the recording papers (1) to (5) by using each of the inks of Examples and Comparative Examples.

With respect to the solid image (3 x 3 cm) of each color, the color-scale values L*, a* and b* according to the color-difference indicating system defined by CIE (Commision International de l'Eclairage) were measured by Macbeth CE-7000 spectrophotometer (manufactured by Macbeth Corp.). The differences between the color-scale values measured and the color reference values of cyan according to ISO 2845-1975, shown below were obtained, and the color difference was calculated by the following equation (i).

Table 2

	L*	a*	b*
Color reference values of cyan	53.9	-19.1	-54.2

Equation (i):

$$\Delta E^*_{ab}=\sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2} \quad \text{(i)}$$

The average value of the color differences ΔE*ab's which were obtained in terms of the images printed on the five recording papers is as shown in Table 3, and the color differences were evaluated in accordance with the following standard. The color differences shown in Table 3 are those values which were obtained in terms of the images printed by using the printer (1). Almost the same values were obtained even in the case where images were printed by using the printer (2).

In the table:

- All of the color differences ΔE*ab's of the images printed on the five recording papers are 20 or less: ◎
- At least one of the color differences is more than 20 and 30 or less: ○
- Only one of the color differences is in excess of 30:△
- Two or more of the color differences are in excess of 30: X

Test A2: Quality of Image

Alphabets and graphic images were printed by the printer (1) and (2) on each of the recording papers (1) to (5) with the inks of Examples and Comparative Examples. These images were visually observed, and evaluated according to the following standard:

- Non-blurred, sharp images having excellent quality: ◎
- Scarcely-blurred, sharp images having good quality: ○
- Scarcely-blurred, but slightly lacked in sharpness: △
- Remarkably-blurred or lacked in sharpness: X

Test A3: Water Resistance

The samples of the solid image printed on the recording paper (3) with the printer (1), obtained in the Test A1 were dipped in tap water for one hour, pulled out, and dried spontaneously. With respect to these samples, the ΔE*ab's were obtained before and after the test in the same manner as in Test A1, and the results were evaluated in accordance with the following standard:

The remaining rate obtainable by the following equation (ii) is:

100 - 90%: ◎
90 - 75%: ○
75 - 60%: △
60% or lower: X

Equation (ii):

$$\text{Remaining Rate (\%)} = \frac{\Delta E^*ab \text{ after the test}}{\Delta E^*ab \text{ before the test}} X\ 100 \qquad \text{(ii)}$$

Test A4: Light Resistance

The samples of the solid image printed on the recording paper (3) with the printer (1), obtained in the Test A1 were placed in a transparent plastic cello case, and allowed to stand under the sunlight for 30 days. With respect to these samples, the ΔE*ab was obtained before and after the test in the same manner as in Test 1, and evaluation was carried out in accordance with the following standard:

The remaining rate obtainable by the above equation (ii) is:

100 - 90%: ◎
90 - 75%: ○
75% or lower: X

The results of the Tests 1 to 4 were as shown in Table 3.

Table 3

Test Item	Ink	Example A										Comparative Example A		
		1	2	3	4	5	6	7	8	9	10	1	2	3
Test 1**	ΔE^*_{ab} Average Value*	28.7	19.8	17.6	12.4	13.0	18.1	17.5	22.1	14.8	16.3	15.2	18.3	16.7
Color Reproducibility	Judgement	○	◎	◎	◎	◎	◎	◎	○	◎	◎	◎	○	◎
Test 2** Quality of Image	(1)	◎	◎	◎	○	◎	◎	◎	◎	◎	◎	◎	◎	◎
	(2)	△	○	◎	○	◎	○	◎	◎	◎	◎	◎	△	△
	(3)	○	◎	◎	○	◎	◎	◎	◎	◎	◎	◎	○	○
	(4)	○	◎	◎	○	◎	◎	◎	◎	◎	◎	◎	○	○
	(5)	○	◎	◎	△	◎	◎	◎	◎	◎	◎	◎	○	○
Test 3	Water Resistance	◎	◎	◎	○	◎	◎	◎	◎	◎	◎	×	△	△
Test 4	Light Resistance	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	×	○	○

*: The color differences in Test 1 are those values which were obtained in terms of the images printed with the printer (1); almost the same values can be obtained even in the case where images are printed with the printer (2).

**: In Tests 1 and 2, the judgments on the images printed with the printer (1) were equal to those on the images printed with the printer (2).

Example B

Yellow, magenta and cyan inks, each having the composition shown in the following Table 4 were prepared in a conventional manner.

In the table, figures are in "% by weight" of the ink composition and the balances are water.

Table 4

Formulation of Ink		Example B1		Example B2		Example B3		Comparative Example B1	
Yellow Dye	II-3	1.5							
	III-5			2					
	III-10					0.5			
	C.I. Acid Yellow 23							1.8	
Magenta Dye	IV-5								
	IV-6								
	IV-9								
	C.I. Acid Red 52								
Cyan Dye	I-4								
	I-3								
	I-13								
	C.I. Acid Blue 9								
Diethylene glycol		40	37	30	6	5	12	3.5	10	8	6	6	5
Glycerol					5	5	5	5	10	10	6	5	5
2-Pyrrolidone					5	5	5	5	10	10	6	5	5
Thiodiglycol													
Ethanol					4	4		4					
2-Propanol							6			6	6		
Mildew-Proofing agent		0.3	0.3	0.3									

Table 4 (continuation)

Formulation of Ink		Example B4			Example B5			Example B6			Comparative Example B2		
Yellow Dye	II-2	1.5											
	II-10							0.9					
	III-3				1.2								
	C.I. Direct Yellow 86										1		
Magenta Dye	IV-1		2										
	IV-4								0.9				
	IV-10					1.5							
	C.I. Direct Red 9											3	
Cyan Dye	I-4							1					1
	I-11							3					3
	I-3									2			
	I-15			3									
Ethylene glycol					12	12	7				12	8	7
Polyethylene glycol #200								13	10	8			
Glycerol		3	3	2				10	10	10			
Triethanolamine							1						1
N-Methyl-2-pyrrolidone					3	2.5	2				3	2.5	2
1,3-Dimethyl-2-imidazolidinone		1	1	1							5	5	5
Ethanol								8	8	8			
1-Propanol													
Mildew-Proofing agent					0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

Table 4 (continuation)

Formulation of Ink		Example B7			Example B8			Example B9			Comparative Example B3		
Yellow Dye	II-8	1.4											
	III-5				1								
	III-7							1.6					
	C.I. Acid Yellow 23										1.2		
Magenta Dye	IV-1					1.7							
	IV-8		2										
	IV-9								2				
	C.I. Acid Red 249											1.4	
Cyan Dye	I-1									4.5			
	I-3						3.5						
	I-16			4									
	C.I. Direct Blue 86												2.5
Diethylene glycol		15	13	10	18	15	12				18	16	12
Glycerol								10	10	8			
Diethylene glycol monobutyl ether		15	15	15									
Triethylene glycol monobutyl etyher					8	8	8				8	8	8
Dipropylene glycol monomethyl ether								5	5	5			
Surfynol 465					1	1	1	0.1	0.1	0.1	1	1	1
Mildew-Proofing agent		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

*: Acetylene glycol surface active agent

Table 4 (continuation)

Formulation of Ink		Example B10			Example B11			Example B12			Comparative Example B4		
Yellow Dye	II-3	0.5											
	III-8	0.5						3					
	III-10				1.8						1.8		
Magenta Dye	IV-5		2.2						4				
	IV-9					2.5							
	C.I. Acid Red 289											1.5	
Cyan Dye	I-4			5						8			
	I-13						4						
	C.I. Direct Blue 199												3
Diethylene glycol		20	17	12	10	10	10				10	10	10
1,5-Pentane diol								8	8	8			
1,2,6-Hexane triol		3	3	3									
Glycerol								2	2				
2-Pyrrolidone					6	5	2.5				6	6	3
Triethanolamine				1			1						1
2-Propanol		3.5	3.5	3.5									
Surfynol 465					1.5	1.5	1.5	2	2	2	1.5	1.5	1.5
Duck Algin NSPL (Kibun Food Chemifa K.K.)**								0.005	0.005	0.005			
Mildew-Proofing agent		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

**: Sodium alginate (water-soluble polymer)

Evaluation Test B

The inks of Examples B1 to B12 and of Comparative Examples B1 to B4 were evaluated in terms of the following Tests B1 to B3, with the above printer and recording papers.

Test B1: Color Reproducibility

Solid images (100% duty) of yellow, magenta, cyan, red, green, blue and black were printed with the above printer (1) on each of the recording papers (1) to (5) with the inks of Examples and Comparative Examples. The image of red was obtained by superposing the yellow and magenta inks one over the other; the image of green was obtained by superposing the yellow and cyan inks one over the other; the image of blue was obtained by superposing the magenta and cyan inks one over the other; and the image of black was obtained by superposing the yellow, magenta and cyan inks one over another.

With respect to the solid image (3 x 3 cm) of each color, the color-scale values L*, a* and b* according to the color-difference indicating system defined by CIE (Commision International de l'Eclairage) were measured by a Macbeth CE-7000 spectrophotometer (manufactured by Macbeth Corp.). The differences between the color-scale values measured and the color reference values according to ISO 2845-1975, shown in Table 5 were obtained, and the color difference was calculated by the above equation (i).

Table 5

Color reference values of each color (ISO 2845-1975)							
	yellow	magenta	cyan	red	green	blue	black
L*	90.7	48.4	53.9	47.4	47.6	19.2	28.6
a*	-18.4	78.1	-19.1	70.3	-74.1	35.5	0.1
b*	91.1	-7.1	-54.2	47.5	23.2	-53.0	-2.5

The average value of the color differences ΔE^*ab's which were obtained in terms of the images printed on the papers (1) to (5) was as shown in Table 6. The color reproducibility was evaluated in accordance with the following standard.

- All of the color differences ΔE^*ab's obtained in terms of the images of red, green, cyan and black are 20 or less: ◎
- At least one of the color differences is more than 20 and 30 or less: ○
- At least one of the color differences is in excess of 30:X

The results were as shown in Table 6.

Further, the same test was carried out with the printer (2), and almost the same results as the above were obtained.

Test B2: Water Resistance

The samples of the solid image printed on the recording paper (3), obtained in the Test B1 were dipped in tap water for one hour, pulled out, and dried spontaneously. With respect to these samples, the ΔE^*ab was obtained before and after the test in the same manner as in Test B1, and evaluation was carried out in accordance with the following standard:

The remaining rate obtainable by the above equation (ii) is:

100 - 80% in all of the samples of seven colors: ◎

80 - 60% in all of the samples of seven colors: ○

60% or lower in at least one of the samples of seven colors: X

Test B3: Light Resistance

The samples of the solid image printed on the recording paper (3), obtained in the Test B1 were placed in a transparent plastic cello case, and allowed to stand under the sunlight for 30 days. With respect to these samples, the ΔE^*ab was obtained before and after the test in the same manner as in Test B1, and evaluation was carried out in accordance with the following standard:

The remaining rate obtainable by the above equation (ii) is:

100 - 90% in all of the samples of seven colors: ◎

90 - 75% in all of the samples of seven colors: ○
75% or lower in at least one of the samples of seven colors: X

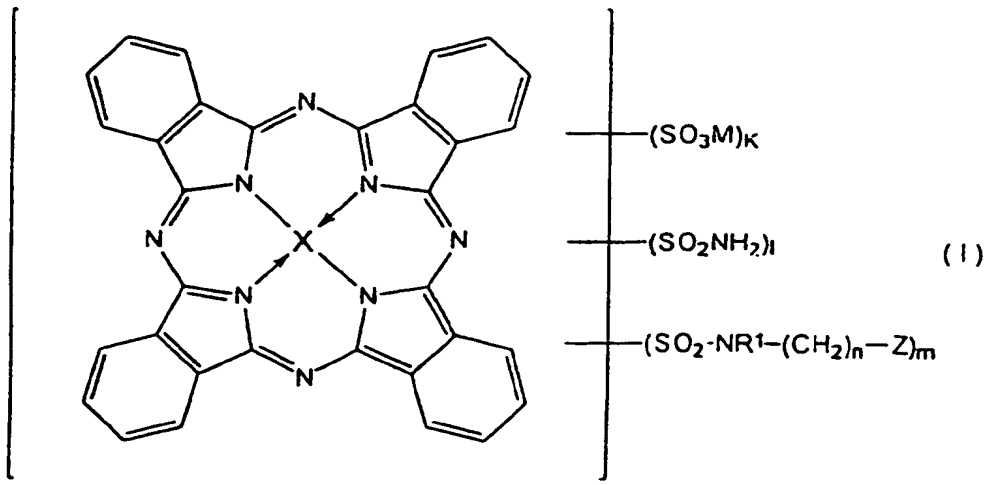
Table 6

Test / Formulation of Ink	Test B1 Color Reproducibility: ΔE* ab (Average value in 5 types of recording papers) Yellow	Magenta	Cyan	Red	Green	Blue	Black	Judgement	Test 2B Water Resistance	Test 3B Light Resistance
Example 1	17.5	16.7	24.6	13.6	17.5	26.8	4.9	○	◎	◎
Example 2	19.8	17.2	19.4	18.2	19.1	18.6	8.0	◎	◎	◎
Example 3	3.2	14.5	13.1	14.8	19.3	22.7	22.4	○	◎	◎
Example 4	15.3	18.0	17.7	19.6	18.8	19.3	19.7	◎	◎	◎
Example 5	8.5	12.2	18.1	18.0	16.2	13.0	17.3	◎	◎	◎
Example 6	5.7	11.8	12.8	20.9	14.4	12.4	20.8	○	◎	◎
Example 7	11.7	19.2	16.5	15.2	17.6	17.2	10.2	◎	◎	◎
Example 8	10.0	17.0	15.6	19.4	14.6	16.7	7.3	◎	◎	◎
Example 9	16.9	16.4	18.0	18.1	19.2	17.1	3.8	◎	◎	◎
Example 10	7.4	16.7	18.3	15.3	8.0	11.6	10.4	◎	◎	◎
Example 11	12.0	18.3	16.9	19.3	15.0	14.2	4.8	◎	◎	◎
Example 12	23.2	20.4	28.8	15.6	17.8	26.3	3.3	○	◎	◎
Comparative Example 1	7.4	21.3	15.7	32.1	36.3	41.2	30.4	×	×	×
Comparative Example 2	19.8	15.3	18.4	30.6	18.8	39.3	28.7	×	×	×
Comparative Example 3	7.0	13.9	15.2	28.4	19.7	40.9	35.0	×	×	×
Comparative Example 4	12.1	24.8	16.7	33.8	27.9	45.1	42.6	×	×	×

*: The values shown in the table are those obtained in terms of the images printed with printer (1). However, almost the same values were obtained even in the case where images were printed with the printer (2).

Claims

1. An ink composition comprising as a colorant a phthalocyanine derivative represented by the formula (I):



(I)

wherein

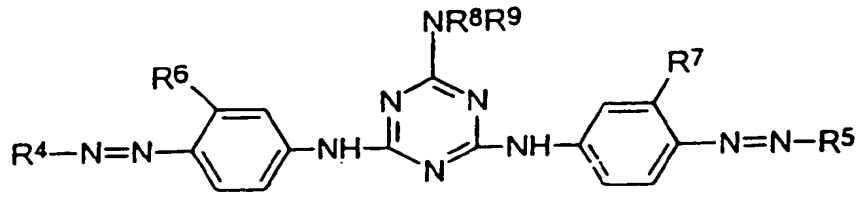
X represents an ion of a metal selected from Cu, Fe, Co and Ni,
M represents hydrogen atom, an alkaline metal, ammonium or an organic amine,
R^1 represents hydrogen atom or an alkyl group which may be substituted,
Z represents -OH, -COOH or NR^2R^3 (where R^2 represents hydrogen atom or an alkyl group which may be substituted, and R^3 represents an alkyl group which may be substituted or phenyl group which may be substituted),
n represents an integer of 1 to 15,
k and l each independently represent 0 or 1, and
m represents an integer of 1 to 4,
provided that k, l and m fulfill the inequality $2 \leq k + l + m \leq 4$.

2. The ink composition according to claim 1, comprising a main solvent which comprises at least water and a water-soluble organic solvent, and from 1.5 to 8.0% by weight of the phthalocyanine derivative represented by the formula (I).

3. The ink composition according to claim 1, for use in ink jet recording.

4. An ink jet recording method comprising the step of ejecting droplets of the ink composition according to claim 1 on a recording medium to form thereon an image.

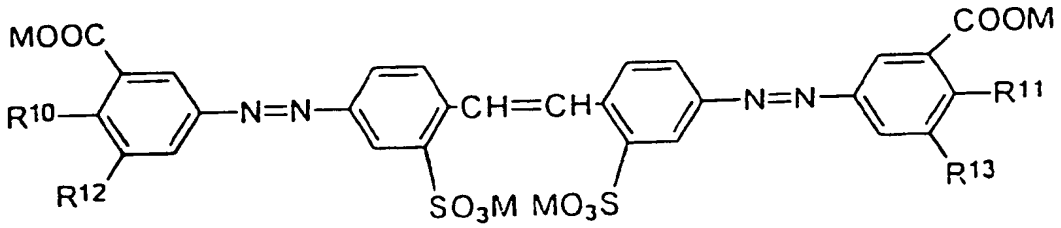
5. A method for forming a color image in which yellow, magenta and cyan ink compositions are used, wherein
the cyan ink composition comprises as a colorant the compound represented by the formula (I) defined in claim 1,
the yellow ink composition comprises as a colorant a compound represented by the formula (II):



(II)

wherein

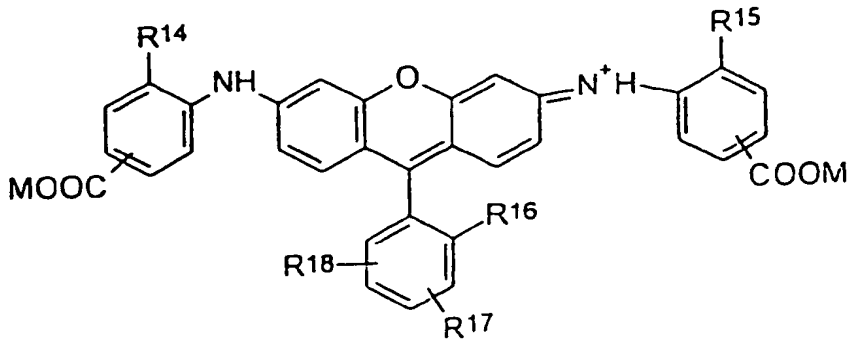
R^4 and R^5 each independently represent -OH, or $-SO_3M$, or phenyl or naphthyl group substituted with -COOM,
R^6 and R^7 each independently represent hydrogen atom, an alkyl group or an alkoxy group,
R^8 represents hydrogen atom, an alkyl group or a hydroxyalkyl group,
R^9 represents hydrogen atom, -OH or a hydroxyalkyl group, and
M is as defined in the above formula (I), or a compound represented by the following formula (III):



(III)

wherein

R^{10} and R^{11} each independently represent hydrogen atom, -OH or an alkoxy group,
R^{12} and R^{13} each independently represent hydrogen atom or an alkyl group, and
M is as defined in the above formula (I), and
the magenta ink composition comprises as a colorant a compound represented by the formula (IV):



(IV)

wherein

R^{14} represents hydrogen atom or an alkyl group,
R^{15} represents hydrogen atom, a halogen atom or an alkyl group,
R^{16} represents -COOH or $-SO_3^-$,
R^{17} and R^{18} each independently represent hydrogen atom, a halogen atom, an alkyl group or $-SO_3M$, and
M is as defined in the above formula (I).

6. The method according to claim 5, wherein
the cyan ink composition comprises 1.5 to 8.0% by weight of the phthalocyanine derivative represented by the formula (I), the yellow ink composition comprises 0.5 to 3.0% by weight of the compound represented by the formula (II) or (III), and
the magenta ink composition comprises 0.5 to 4.0% by weight of the compound represented by the formula (IV).

7. The method according to claim 6, comprising the step of ejecting droplets of the yellow, cyan and magenta ink compositions on a recording medium to form thereon a color image.

8. The method according to claim 7, comprising the step of ejecting droplets of two ink compositions selected from the yellow, cyan and magenta ink compositions on a recording medium to reproduce thereon a color of red, green or blue.

9. The method according to claim 7, comprising the step of ejecting droplets of the yellow, cyan and magenta ink compositions on a recording medium to reproduce thereon a color of black.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP95/00815

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^6 C09D11/00, B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^6 C09D11/00-11/20, B41M5/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 62-34970, A (Bayer AG.), February 14, 1987 (14. 02. 87), Claim & DE, 3600348, A1	1, 2
X	JP, 6-16982, A (Ricoh Co., Ltd.), January 25, 1994 (25. 01. 94), Claim (Family: none)	1 - 4
X	JP, 62-149758, A (Taoka Chemical Co., Ltd.), July 3, 1987 (03. 07. 87), Claim & EP, 196901, A1	1 - 4
X	JP, 59-30874, A (Taoka Chemical Co., Ltd.), February 18, 1984 (18. 02. 84), Claim (Family: none)	1 - 4
X	JP, 59-22967, A (Taoka Chemical Co., Ltd.), February 6, 1984 (06. 02. 84), Claim (Family: none)	1 - 4

☑ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
May 23, 1995 (23. 05. 95)	June 13, 1995 (13. 06. 95)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)